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Methods for Film Coating Electrospun Fibers

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*Research for this project was abruptly stopped and unfinished due to the COVID-19 pandemic.

The completed experiments along with what was planned will be discussed.

Executive Summary

Electrospun membranes have many potential uses in filtration, tissue engineering, drug delivery, and catalysis [2]. Electrospun membranes will have lower tensile strengths but higher malleability than cast films of the same polymer [3]. Joining fibers with a thin film will increase tensile strength compared to just fibers and increase malleability compared to just film.

Three methods of covering electrospun fibers with a film were tested. The first technique involved electrospraying a lower melting point polymer onto the fibers. The sprayed beads were then melted forming a film. Spin coating works by slowly dripping a polymer solution at the axis of rotation of a horizontal layer of a fiber mat sample rotating at a high rotation rate. The solution is forced outwards by the centrifugal force of the rotation. The solvent gradually evaporates leaving a polymer film behind. Dip coating involves immersing the fiber sample in a polymer solution for a set time. The sample is removed and the solvent evaporates leaving a film behind.

Spraying then melting showed the least damage to the electrospun fibers and dip coating showed the most. Ideal setup conditions for electrospinning nylon and for electrospinning and electrospraying PVDF (polyvinylidene fluoride) were found. A solvent mixture of 40 wt% ethanol and 60 wt% acetone was able to dissolve 0.05 wt% PVDF under heat and stirring with minimal damage to electrospun PVDF fibers. Ideal rotation speed for spin coating was found to be 1200 rpm for a 1 cm by 1 cm square fiber sample. Closure of the lab due to the response to

the pandemic prevented characterization of the fiber samples to allow comparisons of the structure, porosity, tensile strength, or contact angles of the membranes. In the results section of the report expected trends for each of the techniques are discussed.

The data that were obtained will facilitate future work and the completion of the project once allowed. Setting up the experiments, electrospinning, solvent optimization, report writing, and research skills were career skills learned from this experience. Personal gains include improved communication and independence. Flexibility was practiced to get a useful report from an experiment that was cut short. The results are limited but can still contribute to science and engineering by allowing future research to be done more effectively. Similar research can improve filtration, tissue engineering, drug delivery, and catalysis.

Future work should finish the experimentation. The first step is optimizing the dip coating parameters. The next step is to produce a similar g/m^2 membrane using each technique. Samples can be cut from the final membrane and characterized by SEM for structure. Image analysis can be performed on the SEM images to find porosity. Tensile strength can be tested by twisting similar weights of membrane into strands and stretching to failure. Contact angles can be found from shapes of water sitting on the sample surfaces. The research can be taken further by testing a gas permeable polymer to relate film thickness to permeability rates. The area of membrane covered by film can be optimized using the electrospray and melt technique. The flow rate of the sprayed polymer can be varied. Other students performing independent research should plan and manage their time effectively. Being flexible and making modifications to experiments along the way can lead to more interesting results.

Introduction

Electrospinning is a process for creating a membrane of around 0.05 to 5 micron thick fibers [1]. A polymer is dissolved in a certain combination of solvents to get a good balance of volatility and viscosity. The solution is loaded into a syringe pump. An electric field of around 10 to 20 kV is applied between the needle of the syringe and the collector. A small droplet forms at the end of the needle. The electric field stretches the polymer solution into a conical shaped drop known as a Taylor cone [1]. Once the voltage is high enough a jet of solution is ejected from the tip of this cone. As the jet travels the solvent evaporates leaving behind a thin polymer fiber. At appropriate polymer-solvent concentrations the jet dries into solid smooth fibers. If the polymer concentration is too low the polymer jet may break up into drops (and hence electrosprays drops) and at intermediate concentrations between spraying drops and forming fibers the jet may form into a fiber – bead structure (like a bead necklace). Electrospinning is capable of producing nonwoven nanofiber membranes out of various polymers. Electrospun membranes have many potential uses in filtration, tissue engineering, drug delivery, and catalysis [2]. Electrospun membranes will have lower tensile strengths than cast films of the same polymer. Some polymers such as PCL are very brittle and crack in film form but are much more malleable as an electrospun fiber membrane [3]. Joining fibers with a thin film will increase tensile strength compared to just fibers and increase malleability compared to just film.

Three methods of producing a supporting film on polymer nanofibers were considered. Electrospraying then melting, spin coating, and dip coating. To electrospray and melt the polymer being sprayed onto the fibers should have a lower melting point than the fiber polymer. The sample is then heated just above the lower melting point to form a film. Spin coating involves rotating a flat fiber sample and slowly dripping the coating material in the center of

rotation. The coating is forced outwards to evenly cover the fibers then dry. The coating is built up over time. Dip coating involves immersing a substrate in a coating solution for a controlled amount of time. The substrate is pulled out and allowed to dry before it is dipped again to build up the coating.

Electrospinning has been researched for decades. Most previous research has focused on the effect of set up parameters such as solvent type, polymer concentration, voltage applied, and needle tip to collector distance. Papers that focus on manipulating the fibers produced using coatings are limited and typically focus on catalysis or drug delivery applications. Coating the fibers in order to balance the tensile strength and flexibility of the membrane is unique.

Experimental Methods

A roller type electrospinning set up with 2 side by side needles was used. The collector was 4 inches in diameter and rotated at 15 rpm. The collector was covered in aluminum foil, ensuring the nonstick coating was facing away from the needles. The distance from needle tip to collector was 4.5in. The voltage applied was set to 25 kV. One syringe pump was set to 35 $\mu\text{L}/\text{min}$ and held both syringes for spraying and spinning. A picture of the electrospinning set up can be seen in Figure 1. The needle tips were moved sideways to cover more of the collector. PVDF and Nylon were the polymers investigated. A solution of 80wt% acetone and 20wt% DMF (Dimehtylformamide) was used to dissolve the PVDF. For nylon a 95wt% HFIP (hexaflouroisopropanol) and 5wt% DMF solution was used. The PVDF solutions were heated to around 40 °C and stirred for at least 2 hours. The Nylon solutions were stirred at room temperature for at least 24 hours.

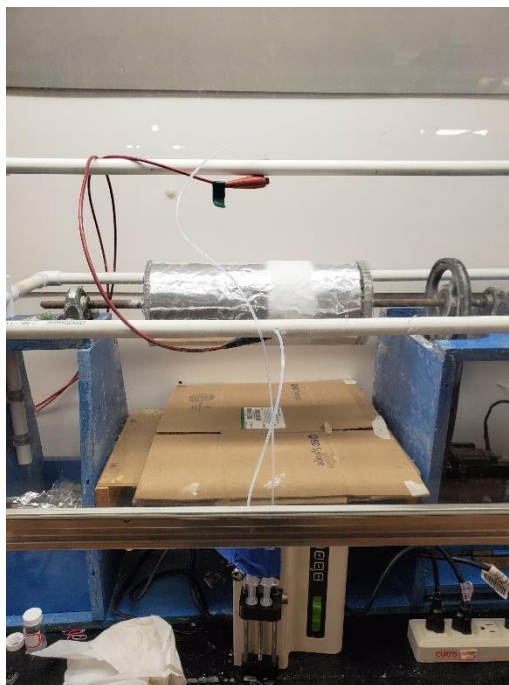


Figure 1: The roller type electrospinning setup used.

The percentage of nylon in a 95 wt% HFIP to 5 wt% DMF solution required to produce fibers was determined first. 3, 5, 7, and 8 wt% nylon solutions were prepared and stirred overnight. The jet was observed against a dark background and in a bright light to check for breakage. A glass slide was also passed under the jet and observed under an optical microscope. The weight per area of the nylon fibers was measured in g/m^2 . Three random 1 cm by 1 cm squares were cut from the membrane. The fibers were peeled from the foil and weighed. Then the average weight was divided by the area. The result was divided by the time the sample was spun so it could be used to estimate the g/m^2 values of other membranes. The percentage of PVDF in a 80 wt% acetone to 20 wt% DMF solution required for fibers and beads was found next. 4 wt% PVDF was tested first. The solution was stirred overnight on a hot plate at around 40 °C. The jet was observed against a dark background and in a bright light. The jet at 4 wt% PVDF was broken. SEM analysis was performed on the resulting membrane. Higher concentrations of

PVDF were also tested to increase the coverage of the film. 10, 15, 20, and 25 wt% PVDF solutions were prepared. The PVDF solutions were spun simultaneously along with the 8 wt% nylon solution. A sample using 20 wt% PVDF on the nylon membrane was heated to 180 °C to melt the PVDF beads but leave the nylon fibers. SEM analysis on these samples but was not completed and is left for future work.

For spin coating and dip coating it was desired to use PVDF for both the film and fibers due to the high cost and limited supply of HFIP solvent required for electrospinning nylon. First a 10 wt% PVDF solution was spun using the same conditions used for nylon. The g/m^2 was measured using the same method as the nylon fibers. It also was divided by time so it could be used to estimate the g/m^2 values of other membranes. In order to apply the film, a solvent that was able to dissolve PVDF under heat and stirring but had little effect on PVDF fibers when dropped on or dipped was desired. Varying concentrations of ethanol and acetone were tested. 10, 20, 30, 40, and 50 wt% ethanol with the balance acetone were tested. Two drops of each solution were dropped from a pipet onto 2 samples of the PVDF fibers. After drying the damage to the membrane was observed. Then 0.5 wt% PVDF was added to each ethanol and acetone solution. The solutions were heated and stirred for up to 48 hours, stopping if clear. After stirring the solvent was allowed to evaporate. PVDF was considered insoluble if powder was visibly left behind after evaporation. It was planned to look at the precipitate under a microscope as well, to check for undissolved PVDF powder, but this was not completed.

For spin coating the 40 wt% ethanol and 60 wt% acetone solution was tested on a 1 cm by 1 cm sample of the 10 wt% PVDF fibers. The fiber sample was peeled from the collector foil and presses flat against a half glass slide. The sample was loaded into the spin coating chamber. The solution was slowly dripped in the center of the sample by a syringe. The rpm started at 500

and was slowly increased until the speed required for the PVDF solution to fully spread across the PVDF fibers. The rpm was further increased in order to spread the film thinner and allow the solution to dry faster. Several samples were planned to be made using a set weight of PVDF solution. 1 cm by 1 cm samples of 10 wt% PVDF fiber were cut to be dip coated in PVDF solution. The time to dip the samples was to be low enough to reduce fiber damage but high enough to fully coat the sample. The number of dips required to achieve the same weight of PVDF as the spin coated sample was to be determined.

SEM analysis was to be performed to characterize the structure and porosity of the optimized membranes from all 3 techniques. Three randomly located samples of each membrane were to be tested at varying SEM magnifications. The tensile strength test was to be performed on set g/m² samples from each technique for a fair comparison. The water contact angle was to be tested to compare the wettability of the resulting membranes. These observations and measurements remain as part of future work.

Data and Results

Several concentrations were tested to optimize the concentration of nylon in the solution used for electrospraying. The jet at 3 wt% was not continuous and was clearly electrospraying. At 5 wt% the jet appeared continuous, but the optical microscope showed large beads and thick broken fibers. At 7 wt% the jet was continuous, and no beads or fiber pieces were visible. 8 wt% nylon was also confirmed to produce fibers and was used for all following experiments. The weight per area of the 8 wt % was 16.8 g/m². The sample was spun for 50 min, giving a value of $20.1 \frac{g}{m^2h}$.

Multiple concentrations of PVDF in solution were tested to find the concentration ranges to produce fibers and beads. For the 4 wt% PVDF solution sprayed on the 8 wt% nylon solution,

beads were formed on the nylon fiber but were sparse, as seen in Figure 2 below. The 10% PVDF jet was observed to be continuous and was electrospinning. The 15% PVDF also appeared to be electrospinning. At 20% the jet was not continuous and was electrospraying. At 25% the jet broke up but PVDF accumulated at the tip of the needle as seen in Figure 3 below.

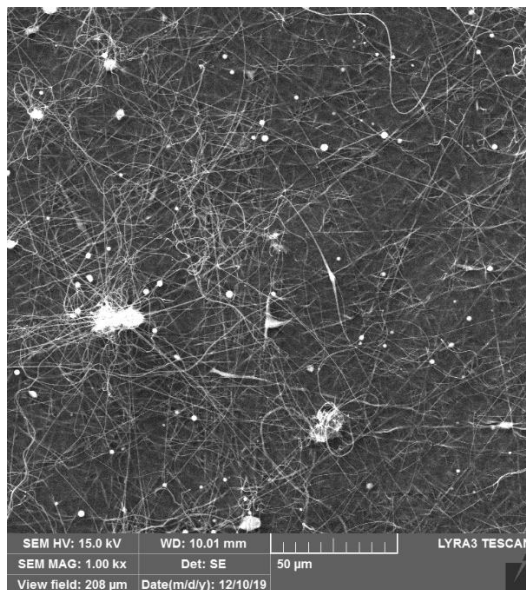


Figure 2: Structure and SEM data of 8 wt% nylon fiber with 4 wt% PVDF spray. The nylon can be seen as long fibers with the PVDF attached as beads.

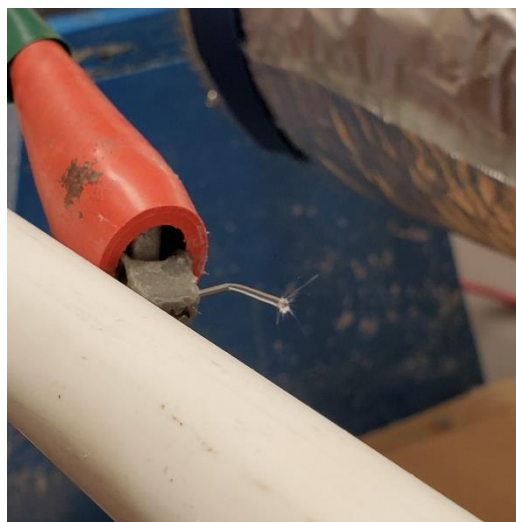


Figure 3: 25 wt% PVDF accumulation at needle tip.

The weight per area of the 10 wt % PVDF fibers was 8.0 g/m^2 . The sample was spun for 65 min, giving a value of $7.4 \frac{\text{g}}{\text{m}^2\text{h}}$. Based on Figure 4 below, it was found that the higher the concentration of ethanol in the PVDF solution the less damage occurred to the fibers. The 0.5 wt% PVDF dissolved fully in all except the 50 wt% ethanol solution. The ideal ratio was determined to be 40 wt% ethanol to 60 wt% acetone for a 0.5 wt% PVDF coating solution. The optimal speed of revolution for a 1 cm by 1 cm sample of 10 wt% PVDF fiber was found. At 900 rpm the PVDF solution fully spread across the 1 cm by 1 cm square sample. This was increased further to 1200 rpm to spread the film thoroughly and allow for the solvent to evaporate faster.



Figure 4: Results of dripping 2 drops of 20, 30, 40 wt% ethanol mixed with acetone on the 10 wt% PVDF fibers

The optimum immersion time and required number of dips for dip coating wasn't determined. Final characterization of membrane samples from each technique wasn't completed.

SEM structure, SEM porosity, tensile strength, and contact angle values, if available, would be used to compare the products of spraying then melting, spin coating, and dip coating.

Discussion

Each film coating technique has strengths and weaknesses. Spraying and melting allows the film to be noncontinuous and dispersed across the fiber network. Not covering all fibers with film will greatly increase the porosity. Higher porosity may be beneficial for some applications such as filtration. Less film will decrease the tensile strength of the membrane but make it more malleable. Requiring polymers with different melting points complicates this technique. Since solvent is evaporated before reaching the membrane damage to the fibers is minimal. If the melting points of the polymers chosen are too similar the fibers will flatten and change structure. It is recommended to use a separate syringe pump for the sprayed polymer so the amount of film can be adjusted.

Spin coating and dip coating will both make an even film across the fibers. A majority of the surface will be covered and porosity will be low. A permeable polymer can be used as the film for gas filtration. A complete film gives a higher tensile strength but lower malleability. If a properly selective solvent is used, the same polymer can be used for the film and the fibers. Solvent damage caused by spin coating can be minimized by adding the film solution slowly and drying between additions. Dip coating will likely cause significant damage to the fibers since it requires full immersion. Using different polymers in solutions that won't dissolve the other would greatly decrease the potential to damage the fibers. Spin coating requires a high revolution rate to fully cover a larger sample of fibers. Dip coating is simple to scale up and is used in many larger scale applications.

Final characterization was not completed and the stated trends aren't backed by data. The conclusive results of the experiment are limited. The data that was obtained will facilitate others to finish the work in the future. Useful data includes the polymer concentrations and other setup conditions required for electrospinning and electrospraying nylon and PVDF. The solvent combination and ratio of ethanol and acetone to selectively dissolve PVDF can be applied to many applications. In order to have conclusive results the experiment should be continued and characterization of samples from each technique compared.

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